Pergamon

Tetrahedron 54 (1998) 15469–15488

TETRAHEDRON

Hydroboration of vinyl silanes with *bis*-(pentafluorophenyl)borane: ground state β-silicon effects.

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Received 5 August 1998; revised 16 October 1998; accepted 17 October 1998

Abstract

Hydroboration of aliphatic vinyl silanes with the highly electrophilic *bis*-(pentafluorophenyl)borane, $HB(C_6F_5)_2$, gives predominantly the thermodynamically favored regioisomer with boron and silicon on the same carbon. Thermodynamic product mixtures are obtained because equilibration of isomers through boryl migration is facile in the products of hydroboration with $HB(C_6F_5)_2$. The 1,1-substituted isomers are the most stable by virtue of a ground state β-silicon effect involving hyperconjugation between the Me_3Si group and the electrophilic borane center. More complex thermal rearrangements are observed when aromatic vinyl silanes are hydroborated with $HB(C_6F_5)_2$. Experiments using ^{13}C-labelled and *para*-substitituted substrates provide mechanistic information on these rearrangements which appear to be driven by the formation of compounds which can engage in the ground state β-silicon interaction. The mechanistic proposals given are supported by computational results performed at the AM1 level.

Keywords: Boron and compounds; Hydroboration; Silicon and compounds; Olefins

1. Introduction.

Vinyl silanes have long been recognized as being special substrates for the hydroboration reaction in that, depending on the borane reagent, unusual regioselectivities can be obtained. Seyferth originally reported on the hydroboration of vinyltrimethylsilane using "BH_3" and found that the 1-trimethylsilyl and 2-trimethylsilylethanol isomers were produced in a roughly 60:40 ratio after work-up [1], suggesting a regiochemical preference for the 1-bora-1-sila-substituted hydroboration product.

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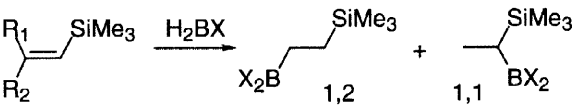
0040-4020/98/$ - see front matter
PII: S0040-4020(98)01008-4

Since then, several studies have reported on the hydroboration of this and other vinylsilane substrates using a variety of borane reagents [2]. In general, these reactions are kinetically controlled and the outcomes can be rationalized on the basis of steric arguments. For example,

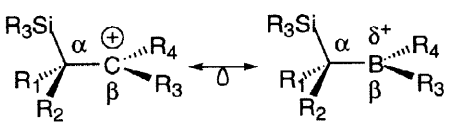
Scheme 1



R_1	R_2	X	1,2:1,1
H	H	H	43:57
		IPC	55:45
H	Me	H	5:95
		IPC	4:94
Me	Me	H	2:98
		IPC	2:98

as the data shown in Scheme 1 demonstrates, the 1,1 products of hydroboration can be formed exclusively by placing methyl substituents on the 2-carbon of the vinylsilane C=C double bond. In the parent, unsubstituted vinyl silane, use of bulkier borane reagents tends to favor the 1,2 products as demonstrated by the outcomes of hydroboration of vinylsilane with "BH_3" vs $IPCBH_2$ (IPC = isopinocampheyl). Use of even bulkier diorganoboranes invariably produces the 1,2 isomer exclusively[3].

It could be argued on the basis of the well known β-silicon effect for the stabilization of carbocations [4] that the 1,1 substituted isomers should be thermodynamically favored over the (apparently) more sterically open 1,2 isomers, since boranes are isoelectronic with carbocations (**I** and **II**). Hyperconjugation between the Si-C bond and the empty p-orbital on the borane should provide for stabilization of the ground state of the 1,1 isomer relative to the 1,2 isomer provided the counterbalancing steric repulsions between BR_2 and SiR_3 are not too severe. In fact, the steric requirements of the Me_3Si group are markedly lower than related hydrocarbyl substituents given the longer Si-C bond, so these $BR_2/SiMe_3$ interactions are not as severe as one might think. If a viable low energy equilibration pathway were available for isomer interconversion, reactions regioselective for the 1,1 isomer might therefore be observable.



I II

We recently reported the new hydroboration reagent $HB(C_6F_5)_2$, **1** [5]. In addition to being highly reactive towards olefins, we found that boryl migration in the product boranes is much more facile than for other BR_2 fragments, provided β-hydrogens are present. The boryl migration likely takes place via a retrohydroboration/rehydroboration sequence, which represents an equilibration pathway which should allow for access to the most thermodynamically favored of available isomers. Furthermore, given the high electrophilicity imparted to the boron center by the electron withdrawing C_6F_5 groups, the strength of the

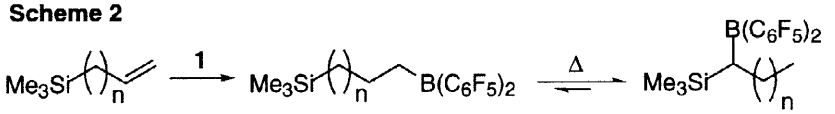
boron/silicon interaction (**II**) ought to be greater than for other BR_2 groups. In fact, we noticed this effect in the dihydroboration of $Me_3SiCH_3{\equiv}CH$ with **1** [5a]; this observation prompted us to examine the reactions of **1** with a variety of silylated olefins and the results are described herein.

2. Results and Discussion.

2.1 Hydroboration of aliphatic trimethylsilyl alkenes.

To assess the directing ability of the Me_3Si group in hydroborations with **1**, we first examined the reactions of **1** with vinyltrimethylsilane, allyltrimethylsilane and 6-trimethylsilyl-1-hexene (Scheme 2). In each substrate, the predominant product under kinetic conditions is the

Scheme 2



		Ratios		
		Kinetic	Therm	
n = 0	**2**	96:4	13:87	**3**
n = 1	**4**	100:0	12:88	**5**
n = 4	**6**	100:0	15:85	**7**

regioisomer derived from anti-Markovnikov addition of B-H to the C=C double bond, *i.e.*, the terminal isomers **2**, **4**, and **6**. Upon thermal equilibration, each of these compounds isomerize to a thermodynamic mixture of the terminal boryl isomers and the isomers with the $B(C_6F_5)_2$ group β to the silicon atom (**3**, **5**, and **7**). In the case of vinyl silane, the predominance of **3** in the final product mixture contrasts sharply with the results of hydroboration with other diorganoboranes of comparable steric bulk to **1** [3].

The final ratio of isomers is roughly the same in each case, favoring the 1,1 isomer by about 6:1. During the isomerization of **4** → **4**:**5** and **6** → **6**:**7**, no isomers with the boryl moiety along the alkyl chain are observed, indicating that once the boryl group moves out of the terminal position migration to either end of the chain is rapid under the conditions employed. The equilibrium mixture of **6**:**7** can also be obtained by hydroboration of (*Z*)-1-trimethylsilyl-1-hexene and thermal equilibration of the kinetic product mixture, which consists of about a 2:1 mixture of **7** and other isomers.

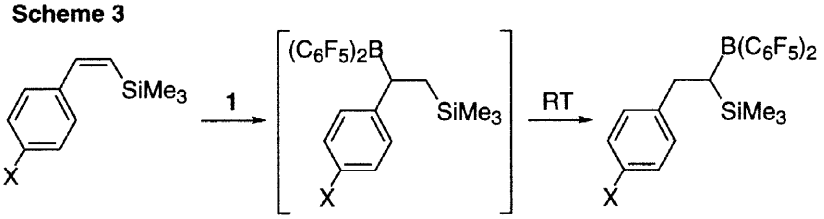
Attempts to study the equilibrium of involving **2** and **3** over a range of temperatures (80-120°C) showed that the ratio is essentially invariant between these limits even with long equilibration times allowed. A K_{eq} of 6-7 corresponds to a ΔG° of about 1.5 kcal mol^{-1}, which is probably a good estimate of ΔH° given that ΔS° should be close to 0 for this equilibrium; it is therefore not surprising that the equilibrium is not very sensitive to changes in temperature. Since the equilibrium is not more completely shifted towards the 1,1 isomers, the energetic benefit of the ground state β silicon effect in these compounds is not substantial enough to fully counteract the unfavorable steric interactions between the geminal Me_3Si and $B(C_6F_5)_2$ group.

Nonetheless, the 1,1 isomers are favored in this equilibrium, indicating that the β-silicon effect in these compounds must provide at least 1.5 kcal mol^{-1} in stabilization.

2.2 Hydroboration of aryl substituted vinylsilanes.

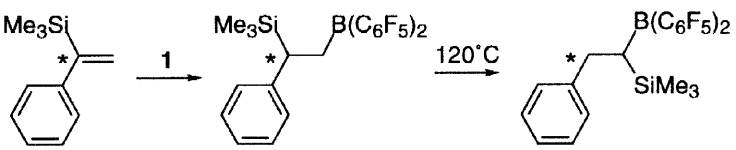
We reasoned that more selective reactions may be observed in substrates which lack β-hydrogens around the double bond. (*Z*)-aryl substituted vinyl silanes **8a-d** were therefore subjected to hydroboration with **1** (Scheme 3). For X = H or F, a mixture of the vicinal (**9a'**, **9d'**) and geminal (**9a**, **9d**) isomers is initially produced, slightly favouring the former. At room temperature these mixtures gradually convert to the 1,1 substituted compounds exclusively. For

Scheme 3



		Kinetic Ratio **9':9**		Therm Ratio **9':9**	
X = H	**8a**	**9a'**	55:45	**9a**	0:100
X = Me	**8b**	**9b'**	0:100	**9b**	0:100
X = OMe	**8c**	**9c'**	0:100	**9c**	0:100
X = F	**8d**	**9d'**	60:40	**9d**	0:100

Scheme 4



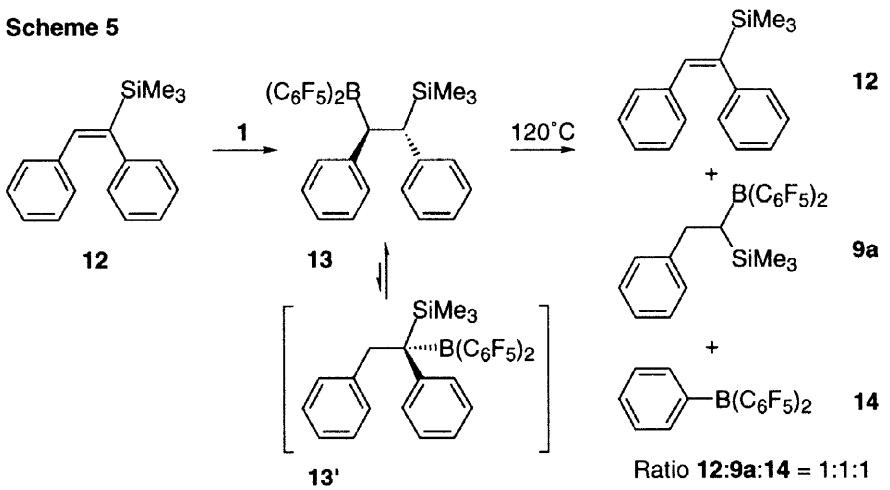
10 **11** **9a**

the substrates with electron donating groups in the *para* position, the 1,2 isomers are not detected. Thus, for X = Me or OMe, either isomerization from the 1,2 to the 1,1 isomer is much more rapid, or the donor properties of the X substituent enhances kinetic selectivity of H-B addition to the C=C double bond. The latter would be consistent with the accepted picture of the polarity of the 4-centered transition state for hydroboration [6]. At any rate, for substrates of this type, 100% regioselectivity is possible by virtue of the facility of $B(C_6F_5)_2$ migration and the thermodynamic advantage provided by the ground state β-silicon effect. With other hydroboration reagents, the lack of low energy equilibration pathways means that regioselectivity is dictated largely by kinetic and not thermodynamic factors.

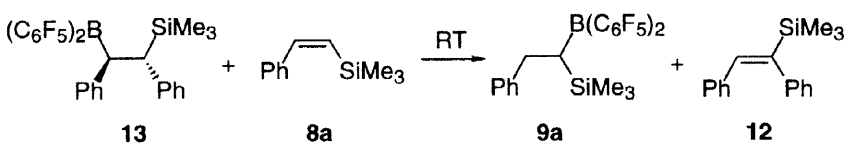
The substrates **8a-d** illustrate a straightforward case of how to utilize the interaction between $B(C_6F_5)_2$ and $SiMe_3$ to effect regioselective hydroborations. Other substrates bring to light the steric limitations of this approach, but also show that rearrangements which do not involve

retrohydroboration/rehydroboration occur to allow the boron and silicon groups to migrate to the same carbon and take advantage of the β-silicon effect. For example, 1-phenyl-1-trimethylsilylethene **10** is rapidly hydroborated regioselectively to borane **11** (Scheme 4) in a reaction whose outcome is probably dictated by sterics. When subjected to thermal equilibration at 120°C, boryl migration to the 1-carbon is not observed; rather, an isomerization to borane **9a** occurs quantitatively over the course of several hours. This surprising observation requires that either the phenyl and $B(C_6F_5)_2$ groups exchange sites, or the Me_3Si group undergoes a 1,2 shift of some kind. Experiments where the 1-carbon is selectively ^{13}C labelled[2] in substrate **10** (as indicated by the "*" in the Scheme) show that, formally at least, it is the Me_3Si substitutent which migrates, since the label remains in the benzylic position. The mechanistic implications of this observation will be discussed in more detail below.

Scheme 5



Scheme 6



Hydroboration reactions using diaryl substituted vinyl silanes were examined next. (*Z*)-1,2-diphenyl-1-trimethylsilylethene, **12**, reacted rapidly with **1** to produce borane **13** (Scheme 5). Upon heating, a product mixture consisting of starting olefin **12**, boryl silane **9a** and phenyl-*bis*-(pentafluorophenyl)borane **14** in a 1:1:1 ratio is observed. Assuming that elimination of $PhB(C_6F_5)_2$ from **13** is the first step in this reaction, the observed stoichiometry suggests that the olefin resulting from elimination (*i.e.*, (*E*/*Z*)-**8a**) reacts with **13** to produce **12** and borane **9a**. This is a reasonable postulate since, under these conditions, retrohydroboration of **1** from **13** should be facile. Indeed, if *in situ* generated **13** is treated with vinylsilane **8a** at room temperature, immediate production of the **12**/**9a** mixture is observed (Scheme 6).

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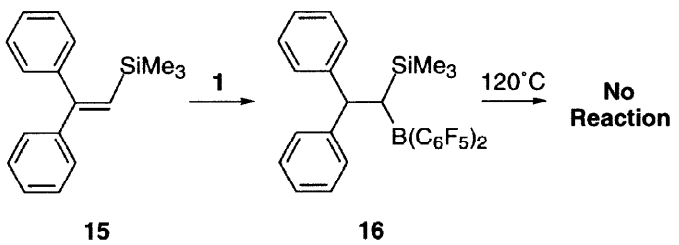
[2] Attempts to follow the deuterium label in d_1-**11**, formed from **10** and d_1-**1** failed to give any information on this process, since the deuterium label is readily scrambled under the conditions employed. Since scrambling occurs prior to product formation, it likely proceeds through $PhC[B(C_6F_5)_2](SiMe_3)CH_2D$ formed via retrohydroboration/rehydroboration from **11**.

The chemistry of Scheme 5 thus appears to begin with endothermic elimination of $PhB(C_6F_5)_2$ from the hydroboration product **13**. The question arises as to whether it is the geminal or the vicinal (relative to the $B(C_6F_5)_2$ moiety) phenyl group which is eliminated. The substrate 1-trimethylsilyl-2,2-diphenylethene, **15**, is hydroborated regiospecifically to the borane **16** (Scheme 7), which is thermally stable for days at 120°C, suggesting that in order to eliminate **14**, the aryl group must be on the same carbon as the boryl group. However, since it is possible that elimination of **14** from **13** could proceed via the regioisomer of **13** obtained via boryl migration (*i.e.*, **13'** Scheme 5),[2] we decided to address this question more concretely by using two series of *para*-substituted diaryl vinylsilanes. In addition to identifying the source of the eliminated aryl group, relative rates of elimination as a function of the electronic properties of the *para* substituent provide useful mechanistic insight into the process.

Scheme 7

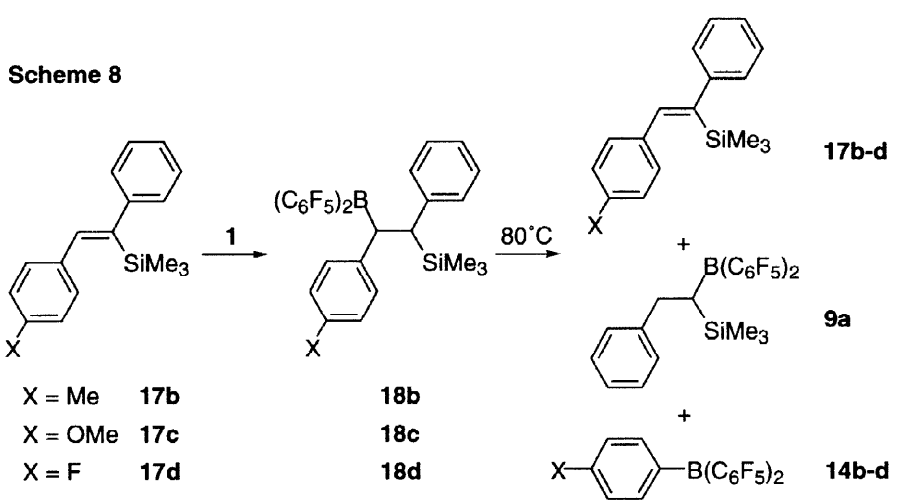


15 **16**

The substrates **17b-d** and **19b-d** (Schemes 8 and 9) were prepared using literature methodology and fully characterized (see Experimental section). Hydroboration produces the silaboranes **18b-d** and **20b-d** exclusively, which were then thermolyzed at 80°C. In the former series, where the *para*-substituted aryl group is geminal to the $B(C_6F_5)_2$ fragment, the eliminated aryl-$B(C_6F_5)_2$ contains the substituent, while **9a** is the only borasilane product present in the resulting product mixtures. Conversely, when **20b-d** are subjected to thermal duress, unsubstituted **14** is the sole elimination product, while borasilanes **9b-d** (identified spectroscopically by comparison to the products of Scheme 3 above) are produced depending on the particular substitutent involved. Thus, the aryl group geminal to the $B(C_6F_5)_2$ fragment is exclusively eliminated in this reaction.

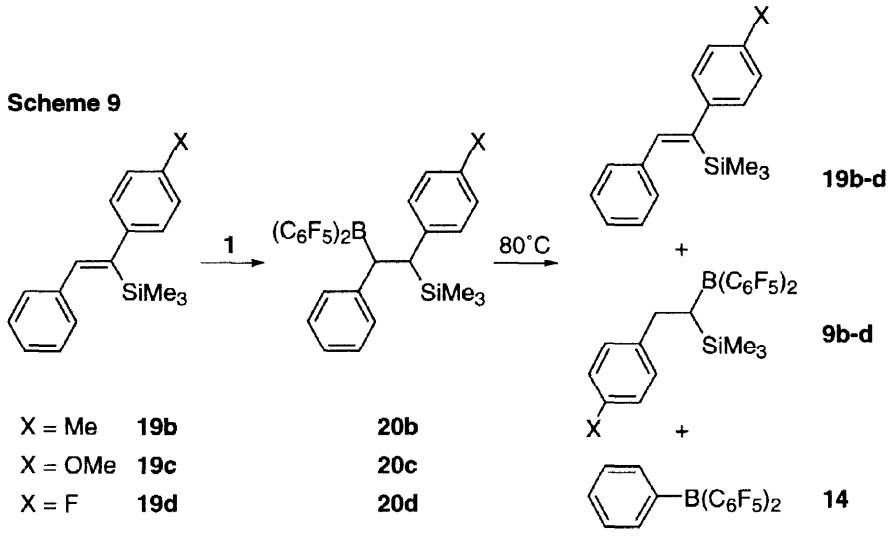
In order to assess the relative rates of this process as a function of the X substituent, samples

Scheme 8



X = Me **17b** **18b**
X = OMe **17c** **18c**
X = F **17d** **18d**

Scheme 9



of silaboranes **18b-d** and **20b-d** were prepared such that they were of equal concentration. The six samples were then heated simultaneously and the progress of the elimination monitored by ^{1}H NMR spectroscopy. Within both series of compounds, the relative rates are dependent upon the ability of X to donate electron density via resonance, *i.e.*, OMe > F > Me. A comparison of the relative rates between the two series of compounds shows that, for a given X substituent, compounds **20** react faster than the corresponding isomer in compounds **18**. Thus, substitution on the aryl group which is *not* eliminated has a greater effect on the overall rate of the process.

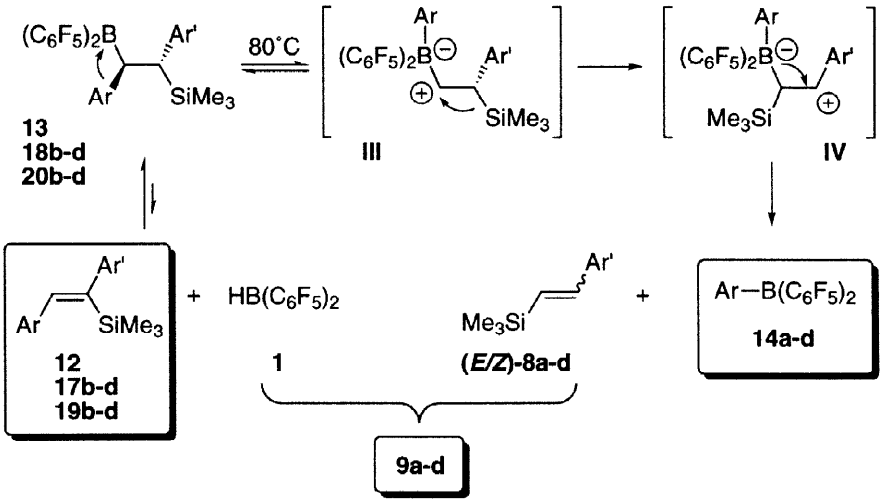
Table 1

Select Parameters of AM1 Optimized Structures of Borane **13** and Transition State Between **13** and Intermediate **III**.

Parameter[a]	**13**	Transition State	Δ_p[b]
ΔH_f (kcal mol^{-1})	-345.55	-301.42	44.13
$R_{Ci\text{-}C\alpha}$ (Å)	1.4914	1.9299	0.4385
$R_{Ci\text{-}B}$ (Å)	2.5566	1.6599	-0.8967
$R_{C\alpha\text{-}B}$ (Å)	1.5595	1.5360	-0.0235
q_{Ci} (e)	-0.07	-0.22	-0.15
q_o, q_m, q_p (e)	-0.12,-0.13,-0.13	-0.05,-0.16,-0.07	0.07,-0.03,0.06
$q_{C\alpha}$ (e)	-0.07	0.08	0.21
q_B (e)0.44	0.15	-0.29	
q_{Si} (e)	1.23	1.28	0.05

[a] C_i, C_o, C_m, C_p = *ipso*, *ortho*, *meta*, and *para*-carbons of migrating phenyl.
[b] Δ_p = TS parameter - **13** parameter.

Scheme 10



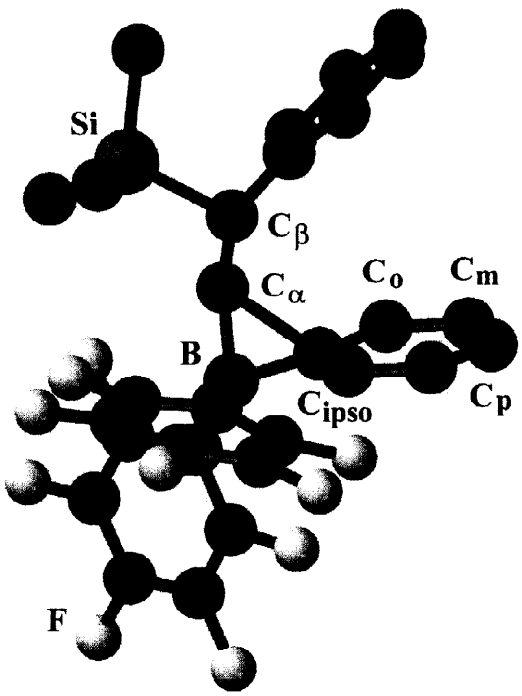
2.3 *Mechanism.*

A mechanism which accounts for these observations is given in Scheme 10. The first step involves Ar migration from the α-carbon to boron which leads to the zwitterionic ylide intermediate **III**. The carbocation formed is stabilized electrostatically by the adjacent borate counterion as well as through the β-silicon effect from the trimethylsilyl substituent. Likely this step is reversible under the conditions employed, since alkyl and aryl migrations from borate boron centers to α-carbons have ample precedent in, for example, the stereospecific synthesis of olefins from alkynyl borates and an electrophile [7]. The analogous reaction of vinyl borates is less common, but has also been observed [8].

Support for such a picture of the reaction was garnered through semi-empirical modeling of the transition state for the phenyl migration step at the AM1 level using the commercially available Spartan suite of programs as described in the Experimental section. The structure of the calculated transition state between **13** and intermediate **III** is shown in Figure 1, while relevant parameters associated with borane **13** and this transition state are given in Table 1, along with the difference between the parameters given for the two structures.

As is apparent from the structure in Figure 1, the transition state resembles a phenonium ion. On going from **13** to the transition state of Figure 1, the C_{α}-C_{ipso} bond length increases while the B-C_{ipso} shortens, such that the migrating phenyl group is almost equidistant from the two atoms. The calculated C_{ipso}-C_{ortho}, C_{ortho}-C_{meta} and C_{meta}-C_{para} distances (averaged) are 1.407, 1.395 and 1.396Å, respectively. Positive charge delocalization into the migrating phenyl group is demonstrated by the increased charge on both C_{para} and C_{ortho}, while the increased negative charge density on B and C_{ipso} is consistent with incipient bond formation. The shortening of the B-C_{α} bond may be indicative of the development of an electrostatic interaction between these two atoms as the charge separation increases. A slight increase in the positive charge associated

Figure 1. Semi-Empirical (AM1) Transition State for Phenyl Migration in **13** → **III.**



with the silicon atom and the orientation of the Me_3Si group indicates that the β-silicon effect is acting to stabilize the developing positive charge at C_α to some extent. Note that the orientation of the Me_3Si with respect to the plane of the developing carbocation at C_α is as would be expected for hyperconjugative stabilization.

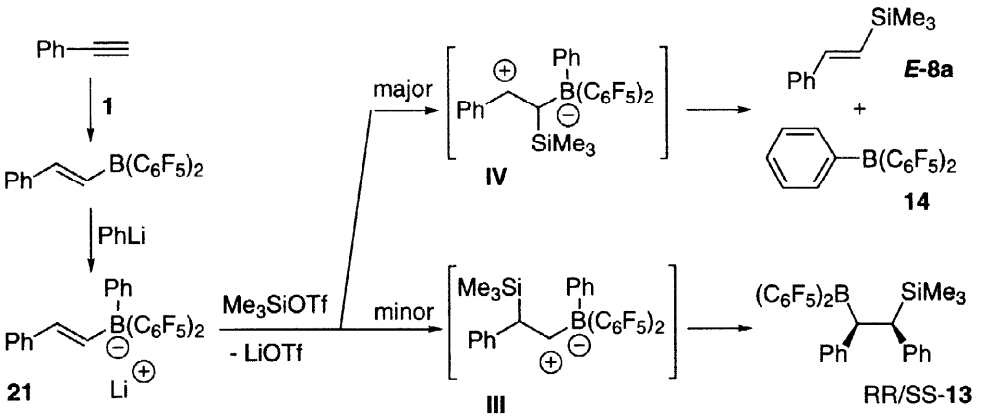
The substituent effects on migration of the Ar group are consistent with this picture of the transition state, where the developing positive charge is delocalized throughout the aromatic ring. In such a transition state, groups capable of electron donation through resonance should have a stabilizing influence. Clearly, the OMe group is the best resonance donor, accounting for the relatively large effect this group has on the rate of migration. Although a fluoro substituent is usually thought of as an electron withdrawer, it does so inductively; in situations of high electron demand, it is capable of electron donation through resonance [9]. Indeed, it is more effective in this role than the Me substituent, accounting for the somewhat counterintuitive rate trend observed for these two groups.

Turning back to Scheme 10, reversible formation of intermediate **III** is followed by migration of the Me_3Si group to form benzylic cation **IV** in a 1,2-sila-Wagner-Meerwein rearrangement [10],[11]. Likely, this is the rate determining step in the reaction. Species **IV** immediately collapses to **14** and the monoaryl vinylsilane product, which triggers the formation of the other observed products as shown above in Scheme 6. Resonance donating substitutents in the *para* position of the Ar' group would stabilize this benzylic cation, and since this is the highest

energy step, these effects would be expected to more pronounced than the substituent effects on the Ar migration step, as is observed.

Attempts to model the Me_3Si migration step failed to find a stable minimum for **IV** indicating that it is likely not a true intermediate in the process, and that loss of $PhB(C_6F_5)_2$ from **IV** occurs concommitantly with silyl migration with a negligible barrier. This is also consistant with the notion that this step is the rate determining part of the process. It is possible, however, to

Scheme 11



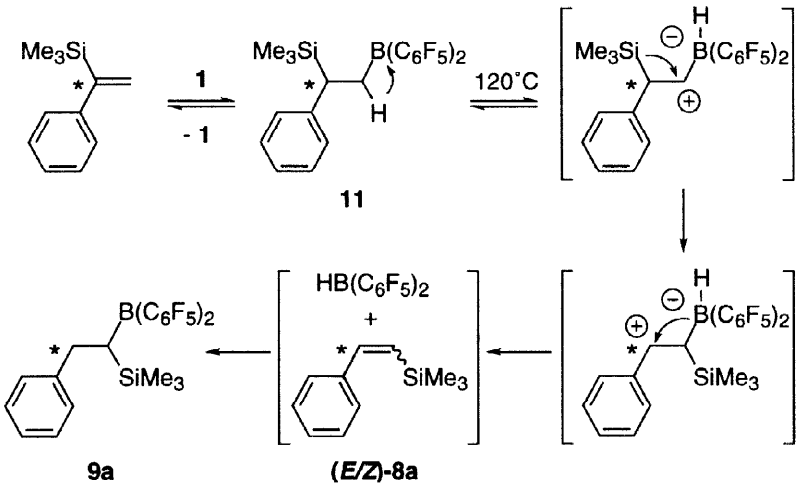
implicate species **IV** chemically in a separate series of experiments as depicted in Scheme 11. Hydroboration of phenylacetylene leads to the vinylborane shown [5a], which, when treated with PhLi, gives borate **21**. This vinylborate is related to that which would obtain if "Me_3Si^+" formally dissociated from species **IV**; thus, **IV** can be potentially generated *in situ* by treatment of **21** with a source of "Me_3Si^+". Accordingly, when **21** is treated with Me_3SiOTf, the majority of the product mixture is comprised of (*E*)-**8a** and **14**, with about 20% of the RR/SS diastereomer of **13** present. Addition of "Me_3Si^+" to the α-vinyl carbon generates **IV** *in situ*, which immediately yields the products of $PhB(C_6F_5)_2$ loss. The proportion of electrophile which adds to the β-vinyl carbon gives a carbocation analogous to **III** which would be expected to rapidly transfer a phenyl group from boron to carbon at room temperature. Hence, the diastereomer of **13** is also observed in the product mixture of this reaction.

The observations concerning the rearrangement of Scheme 4 discussed above can now be accounted for by invoking an H^- transfer instead of aryl migration (Scheme 12). Although retrohydroboration through β-elimination is much more favorable, at higher temperatures, loss of **1** from **11** by α-elimination becomes competitive. Although this step is also reversible, once the rate-limiting 1,2-Me_3Si shift occurs the rearrangement is essentially complete. This mechanism is thus consistent with the ^{13}C-labelling results.

3. Conclusions.

The high electrophilicity of the $-B(C_6F_5)_2$ group allows for high regioselectivity in the hydroboration of certain vinyl silanes using the reagent $HB(C_6F_5)_2$. For substrates

Scheme 12



RCH=CHSiMe$_3$, the energetic benefit afforded by a ground state β-silicon effect between the trialkylsilyl group and the boron center leads to reactions selective for the 1,1-borasilane products. Even though kinetic product mixtures are produced, the facility of retrohydroboration with this reagent opens a low energy pathway for equilibration to thermodynamically more stable products which is unavailable to other boranes under mild conditions. Furthermore, if R is a group which does not allow for boryl migration (*e.g.* aryl groups), the reactions are highly selective. This chemistry offers access to potentially useful α-silylated alcohols and acyl silanes upon oxidation [5b] of the hydroboration products.

The -B(C$_6$F$_5$)$_2$ is also electrophilic enough to induce H$^-$ or Ar$^-$ migrations from C$_\alpha$ to boron at higher temperatures. These migrations trigger a 1,2-shift of the Me$_3$Si group which ultimately allows for ground state β-silicon interactions to form with the -B(C$_6$F$_5$)$_2$ moities. This chemistry has questionable potential for useful applications but is nonetheless a testament to the thermodynamic favorability of the ground state β-silicon effect in these systems.

4. Experimental Section.

4.1 General.

General methods for the manipulation of compounds have been described previously [12]. Borane **1** was prepared as described elsewhere [5]. Vinyltrimethylsilane and allyltrimethylsilane were purchased from Aldrich Sigma and used as received. The following vinyl silanes were prepared according to literature reports: 6-trimethylsilyl-1-hexene [13],[14]; (*Z*)-1-trimethylsilyl-1-hexene [15]; (*Z*)-1-trimethylsilyl-2-phenylethene, **8a**[16]; (*Z*)-1-trimethylsilyl-2-(4-methylphenyl)ethene, **8b**[17]; (*Z*)-1-trimethylsilyl-2-(4-methoxyphenyl)ethene, **8c** [18]; 1-phenyl-1-trimethylsilylethene, **10**[19]; (*Z*)-1,2-diphenyl-1-trimethylsilylethene, **12**, and 1-trimethylsilyl-2,2-diphenylethene, **15** [20]. ^{13}C-labelled **10** was

prepared from $Ph^{13}C(O)CH_3$ which was purchased from Cambridge Isotopes. The following trimethylsilylalkynes were prepared either by quenching *in situ* generated lithium acetylides with Me_3SiCl or by palladium catalyzed coupling of aryl bromides with $Me_3SiC{\equiv}CH$ [21] and identified through comparison with literature spectral data: 1-trimethylsilyl-1-hexyne [22]; trimethylsilylphenylacetylene, trimethylsilyl(4-methylphenyl)acetylene and trimethylsilyl(4-methoxyphenyl)acetylene [23]; trimethylsilyl(4-fluorophenyl)acetylene [24]. **Phenyl-*bis*-(pentafluorophenyl)borane, 14,** was prepared by reaction between PhLi and $ClB(C_6F_5)_2$ [25] and identified by comparison to literature data [26]. NMR spectroscopy was carried out in C_6D_6 unless otherwise noted. Hydroborations with **1** were carried out as described previously [1] and monitored by ^1H NMR spectroscopy; hydroboration products were characterized by ^1H, ^{13}C, ^{19}F and ^{11}B NMR spectroscopy. ^1H and ^{13}C spectra were referenced internally to solvent resonances. ^{13}C resonances for the C_6F_5 groups in all of the new $-B(C_6F_5)_2$ substituted compounds appearred as multiplets at 146.5±1.0 (C_{ortho}), 143.0±0.7 (C_{meta}), 137.7±0.4 (C_{para}) and 115.4±1.0 (C_{ipso}) ppm. ^{19}F NMR spectra were acquired without proton decoupling and referenced externally to hexafluorobenzene at -163.0 ppm [27]. Signals appearred as multiplets but only chemical shifts are reported. ^{11}B NMR data is reported as the chemical shift relative to external $BF_3{\bullet}Et_2O$ at 0.00 ppm, with the width at half height in Hz given in brackets.

4.2 Hydroboration of Vinyltrimethylsilane.

Vinyltrimethylsilane (15.3 μL, 0.099 mmol) was added to a suspension of **1** (34.3 mg, 0.099 mmol) in C_6D_6, producing boranes **2** and **3** in a 94:6 ratio. NMR data for **2**: ^1H: 1.81 (m, 2H, CH_2B). 0.44 (m, 2H, $SiCH_2$). 0.03 (s, 9H, $SiCH_3$). ^{13}C: 23.3 (B*C*). 8.1 (Si*C*). -2.2 ($SiCH_3$). ^{19}F: -132.2 (F_o). -149.4 (F_p). -163.0 (F_m). ^{11}B: 68.2 (900). This mixture was thermally equilibrated at 120°C for 16 hours resulting in ratio of 13:87 (**2**:**3**). NMR data for **3**: ^1H: 2.50 (q, J = 6.4 Hz, 1H, SiBC*H*); 1.07 (d, 3H, CH_3); 0.08 (s, 9H, $SiCH_3$). ^{13}C: 36.7 (B*C*H, C_2); 11.8 (CH_3); -0.4 ($SiCH_3$). ^{19}F: -132.7 (F_o); -151.2 (F_p); -163.1 (F_m). ^{11}B: 72.2 (650).

4.3 Hydroboration of Allyltrimethylsilane

Allyltrimethylsilane (15.4 μL, 0.097 mmol) was added to a suspension of **1** (33.6 mg, 0.097 mmol) in C_6D_6, producing borane **4** exclusively. NMR data for **4**: ^1H: 2.02 (t, J = 7.5 Hz, 2H, CH_2B); 1.56 (m, 2H, CH_2); 0.59 (m, 2H, $SiCH_2$); -0.04 (s, 9H, $SiCH_3$). ^{13}C: 36.6 (B*C*); 21.0 (CH_2); 19.9 (Si*C*); -1.8 ($SiCH_3$). ^{19}F: -132.4 (F_o); -149.1 (F_p); -162.8 (F_m). ^{11}B: 73.7 (770). The sample was thermally equilibrated at 90°C for 3 hours resulting in a ratio of 12:88 (**4**:**5**). NMR data for **5**: ^1H: 2.55 (dd, J = 3.3 Hz and J = 9.8 Hz, 1H, SiBC*H*); 1.66, 1.55 (m, 2H, CH_2); 0.84 (t, J = 7.3 Hz, 3H, CH_3); -0.05 (s, 9H, $SiCH_3$). ^{13}C: 48.2 (B*C*H); 23.0 (CH_2); 19.1 (CH_3); 0.2 ($SiCH_3$). ^{19}F: -132.8 (F_o); -150.9 (F_p); -162.9 (F_m). ^{11}B: 72.2 (770).

4.4 *Hydroboration of 6-trimethylsilyl-1-hexene*

6-trimethylsilyl-1-hexene (14.7 mg, 0.094 mmol) was added to a suspension of **1** (32.5 mg, 0.094 mmol) in C_6D_6, producing borane **6** exclusively. NMR data for **6**: ^{1}H: 1.92 (t, J = 7.7 Hz, 2H, C*H*$_2$B); 1.50 (tt, J = 7.3, 7.7 Hz, 2H, BCH$_2$C*H*$_2$); 1.37 (m, 2H, C*H*$_2$); 1.31 (m, 4H, C*H*$_2$); 0.48 (m, 2H, SiC*H*$_2$); 0.01 (s, 9H, SiC*H*$_3$). ^{13}C: 33.6, 32.7, 25.2, 24.1 (*C*H$_2$); 32.4 (B*C*); 16.9 (Si*C*); -1.7 (SiCH$_3$). ^{19}F: -132.4 (F$_o$); -149.1 (F$_p$); -162.8 (F$_m$). ^{11}B: 73.6 (900). The sample was thermally equilibrated at 80°C for 18 hours resulting in a ratio of 15:85 (**6**:**7**). NMR data for **7**: ^{1}H: 2.67 (dd, J = 3.0, 9.8 Hz, 1H, BC*H*); 1.78, 1.62 (m, 2H, BCHC*H*$_2$); 1.28, 1.16 (m, 6H, C*H*$_2$); 0.81 (t, J = 6.8 Hz, 3H, C*H*$_3$); -0.02 (s, 9H, SiC*H*$_3$). ^{13}C: 45.9 (BCH); 34.3, 31.8, 29.7, 22.7 (*C*H$_2$); 14.0 (*C*H$_3$); 0.3 (Si*C*H$_3$). ^{19}F: -132.7 (F$_o$); -151.1 (F$_p$); -163.0 (F$_m$). ^{11}B: 71.7 (1000).

4.5 *Preparation of (Z)-1-trimethylsilyl-2-(4-fluorophenyl)ethene,* ***8d***.

This vinyl silane was prepared using a literature procedure [15] from trimethylsilyl(4-fluorophenyl)acetylene (0.30 g, 1.6 mmol). The compound was obtained (0.23 g, 1.2 mmol) as a colourless liquid after workup and purification by vacuum distillation in 77% yield. ^{1}H NMR ($CDCl_3$): 7.34 (d, J = 15.1 Hz, 1H, =C*H*); 7.26 (dd, $^4J_{HF}$ = 5.7 Hz and J = 8.5 Hz, 2H, C*H*$_{aryl}$); 7.02 (dd, $^3J_{HF}$ = 8.7 Hz, 2H, C*H*$_{aryl}$); 5.86 (d, 1H, =C*H*); 0.09 (s, 9H, SiC*H*$_3$). ^{13}C NMR ($CDCl_3$): 162.5 (d, $^1J_{CF}$ = 247.0 Hz, FC$_{ipso}$); 145.6, 133.2 (=*C*H); 136.5 (d, $^4J_{CF}$ = 4.2 Hz, C$_{ipso}$); 130.0 (d, $^3J_{CF}$ = 7.4 Hz, *C*H$_{aryl}$); 115.0 (d, $^2J_{CF}$ = 21.9 Hz, *C*H$_{aryl}$); 0.4 (Si*C*H$_3$). Mass spectrum: 194 (9, M$^+$); 179 (35, M$^+$-CH$_3$); 73 (60, (CH$_3$)$_3$Si$^+$). Exact mass calcd. for $C_{11}H_{15}FSi$: 194.0927. Found: 194.0910.

4.6 *Hydroboration of (Z)-1-trimethylsilyl-2-(4-X-phenyl)ethenes,* ***8a-d***.

Vinyl silanes **8a-d** were hydroborated using ≈ 50 mg of **1** and one equivalent of olefin in C_6D_6. The reactions were monitored by ^{1}H NMR spectroscopy until the kinetic product mixture converted completely to the thermodynamic products **9a-d**. NMR data for **9a**: ^{1}H: 6.98 (m, J = 7.3 Hz, 2H, C*H*$_{meta}$); 6.90 (t, 1H, C*H*$_{para}$); 6.82 (d, J = 7.3 Hz, 2H, C*H*$_{ortho}$); 3.17 (dd, J = 5.1, 10.2 Hz, BC*H*); 2.90 (m, 2H, C*H*$_2$); -0.04 (s, 9H, SiC*H*$_3$). ^{13}C: 143.6 (C$_{ipso}$); 128.5, 127.7, 126.3 (*C*$_6$H$_5$); 44.6 (BCH); 34.1 (*C*H$_2$); 0.2 (Si*C*H$_3$). ^{19}F: -132.9 (F$_o$); -151.2 (F$_p$); -163.2 (F$_m$). ^{11}B: 72.2 (1030). NMR data for **9b**: ^{1}H: 6.83 (d, J = 8.0 Hz, 2H, C*H*$_{aryl}$); 6.75 (d, 2H, C*H*$_{aryl}$); 3.17 (dd, J = 5.1, 10.1 Hz, 1H, BC*H*); 2.91 (m, 2H, C*H*$_2$); 2.04 (s, 3H, C*H*$_3$); -0.02 (s, 9H, SiC*H*$_3$). ^{13}C: 140.7, 135.7 (C$_{ipso}$); 129.2, 127.8 (*C*H$_{aryl}$); 44.8 (BCH); 33.8 (*C*H$_2$); 20.7 (*C*H$_3$); 0.2 (Si*C*H$_3$). ^{19}F: -131.1 (F$_o$); -149.7 (F$_p$); -161.5 (F$_m$). ^{11}B: 72.6 (1350). NMR data for **9c**: ^{1}H: 6.75 (d, J = 8.7 Hz, 2H, C*H*$_{aryl}$); 6.63 (d, 2H, C*H*$_{aryl}$); 3.27 (s, 3H, OC*H*$_3$); 3.15 (dd, J = 5.4, 10.2 Hz, BC*H*); 2.90 (m, 2H, C*H*$_2$); -0.02 (s, 9H, SiC*H*$_3$). ^{13}C: 159.0 (OC$_{ipso}$); 136.1 (C$_{ipso}$); 129.1, 114.6 (*C*H$_{aryl}$); 55.4 (O*C*H$_3$); 45.6 (BCH); 33.7 (*C*H$_2$); 0.7 (Si*C*H$_3$). ^{19}F: -131.0 (F$_o$); -149.4 (F$_p$); -161.5 (F$_m$). ^{11}B: 72.6 (1210). NMR data for **9d**: ^{1}H: 6.66 (dd, $^3J_{HF}$ = 8.5 Hz and J = 8.7 Hz, 2H, C*H*$_{aryl}$); 6.58 (dd, $^4J_{HF}$ = 5.4 Hz and J = 8.7 Hz, 2H, C*H*$_{aryl}$); 3.05 (dd, J = 6.3, 8.8 Hz, BC*H*); 2.78 (m, 2H, C*H*$_2$); -0.05 (s, 9H, SiC*H*$_3$). ^{13}C: 161.7 (d, $^1J_{CF}$ = 245.0 Hz, FC$_{ipso}$); 139.2 (d, $^4J_{CF}$

= 3.4 Hz, C_{ipso}); 129.1 (d, $^3J_{CF}$ = 7.4 Hz, CH_{aryl}); 115.3 (d, $^2J_{CF}$ = 21.0 Hz, CH_{aryl}); 44.8 (B*C*H); 33.3 (CH_2); 0.2 (SiCH_3). ^{19}F: -116.9 (C*F*); -131.2 (F_o); -149.2 (F_p); -161.2 (F_m). ^{11}B: 72.8 (1440).

*4.7 Hydroboration of 1-phenyl-1-trimethylsilylethene, **10**.*

Vinylsilane **10** (28.3 mg, 0.162 mmol) was added to a suspension of **1** (56.0 mg, 0.162 mmol) in C_6D_6 and the product **11** assayed by NMR spectroscopy. NMR data for **11**: ^{1}H: 6.89 (m, J = 7.5 Hz, 2H, CH_{meta}); 6.78 (t, 1H, CH_{para}); 6.72 (d, J = 7.0 Hz, 2H, CH_{ortho}); 2.62 (dd, ^3J_H = 12.5 Hz, $^2J_{gem}$ = 16.1 Hz, 1H, BCH_2); 2.30 (dd, 1H, SiC*H*); 2.14 (dd, ^3J_H = 3.3 Hz, 1H, BCH_2); -0.06 (s, 9H, SiCH_3). ^{13}C: 144.1 (C_{ipso}); 128.4, 127.1, 125.1 (C_6H_5); 32.3 (Si*C*H); 30.7 (BCH_2); -3.4 (SiCH_3). ^{19}F: -131.9 (F_o); -149.9 (F_p); -163.3 (F_m). ^{11}B: 73.0 (1030).

*4.8 Hydroboration of (Z)-1,2-diphenyl-1-trimethylsilylethene, **12**.*

Vinylsilane **12** (37.0 mg, 0.147 mmol) was added to a suspension of **1** (51.0 mg, 0.147 mmol) in C_6D_6 and the product **13** assayed by NMR spectroscopy. NMR data for **13**: ^{1}H: 6.93-6.82 (m, 6H, CH_{aryl}); 6.78 (m, 3H, CH_{aryl}); 6.70 (t, J = 7.3 Hz, 1H, CH_{para}); 4.77 (d, J = 12.3 Hz, 1H, BC*H*); 3.25 (d, 1H, SiC*H*); -0.06 (s, 9H, SiCH_3). ^{13}C: 141.4, 133.7 (C_{ipso}); 132.7, 129.2, 128.5, 128.0, 127.5, 124.9 (CH_{aryl}); 47.2 (B*C*H); 37.3 (Si*C*H); -2.1 (SiCH_3). ^{19}F: -128.9 (F_o); -148.9 (F_p); -162.8 (F_m). ^{11}B: 65.8 (1670).

*4.9 Hydroboration of 1-trimethylsilyl-2,2-diphenylethene, **15**.*

Vinylsilane **15** (36.5 mg, 0.145 mmol) was added to a suspension of **1** (50.0 mg, 0.145 mmol) in C_6D_6 and the product **16** assayed by NMR spectroscopy. NMR data for **16**: ^{1}H: 7.29, 6.98 (d, J = 7.7, 7.7 Hz, 4H, CH_{ortho}); 7.04, 6.77 (m, J = 7.5, 7.7 Hz, 4H, CH_{meta}); 6.92, 6.67 (t, J = 7.3, 7.3 Hz, 2H, CH_{para}); 4.43 (d, J = 11.5 Hz, 1H, C*H*); 4.27 (d, 1H, B*C*H); -0.08 (s, 9H, SiCH_3). ^{13}C: 150.4, 145.8 (C_{ipso}); 129.0, 128.9, 127.8, 126.9, 126.2, 126.0 (CH_{aryl}); 52.6 (*C*H); 47.2 (B*C*H); 1.2 (SiCH_3). ^{19}F: -131.9 (F_o); -149.9 (F_p); -163.1 (F_m). ^{11}B: 78.4 (1280).

*4.10 Preparation of (E)-1-phenyl-1-trimethylsilyl-2-(4-X-phenyl)ethenes, **17b-d**, and (E)-1-phenyl-2-(4-X-phenyl)-2-trimethylsilylethenes, **19b-d**.*

Substituted arylvinyl silanes were prepared by N,N-dimethylacetamide catalyzed addition of catecholborane (HBcat) to a trimethylsilylacetylene using the method of Fu *et al.* [28] with subsequent palladiumcatalyzed coupling of the boronate ester with the appropriate aryl bromide according to Keay's procedure [29] without purification of the catecholborane intermediate. Compounds **17b-d** and **19b-d** were purified by column chromatography, eluting with hexanes.

(E)-1-phenyl-1-trimethylsilyl-2-(4-methylphenyl)ethene, **17b**.

(E)-1-phenyl-1-trimethylsilyl-2-(4-methoxyphenyl)ethene, **17c**.

(E)-1-phenyl-1-trimethylsilyl-2-(4-fluorophenyl)ethene, **17d**.

These three substrates were prepared using the Fu/Keay procedure from the appropriate aryltrimethysilyl acetylene and iodobenzene. **17b**: 4-$MeC_6H_4C{\equiv}CSiMe_3$ (0.26 g, 1.4 mmol) was hydroborated (2.7 mL of 1M HBcat in THF) using DMA (0.1 mL) as catalyst in CH_2Cl_2 (10 mL). The solvent was removed *in vacuo* then $Pd(PPh_3)_4$ (78 mg, 0.07 mmol); toluene/ethanol/water (8/8/2 mL); iodobenzene (0.15 mL, 2.7 mmol); and Na_2CO_3 (0.50 g, 4.7 mmol) were added to the residue. The resulting solution was refluxed for 4 hours which afforded **17b** (0.18 g, 0.67 mmol) as a colourless oil in 49% yield. IR (KBr): 3048 (w); 2951 (m); 1587 (m, C=C); 1506 (m); 1440 (m); 1250 (s); 839 (vs, TMS); 761 (s); 695 (s). ^{1}H NMR ($CDCl_3$): 7.32 (t, J = 7.5 Hz, 2H, C*H*$_{aryl}$); 7.26 (s, 1H, =C*H*); 7.21 (m, 5H, C*H*$_{aryl}$); 7.15 (d, 2H, C*H*$_{aryl}$); 2.37 (s, 3H, C*H*$_3$); -0.04 (s, 9H, SiC*H*$_3$). ^{13}C NMR ($CDCl_3$): 147.6, 146.7, 137.3, and 137.1 (*C*$_{quat}$); 145.3 (=*C*H); 128.8, 128.7, 128.2, 127.4, 125.9 (*C*H$_{aryl}$); 21.4 (*C*H$_3$); 1.0 (Si*C*H$_3$). Mass spectrum: 266 (10, M^+); 251 (8, M^+-CH_3); 73 (100, $(CH_3)_3Si^+$). Exact mass calcd. for $C_{18}H_{22}Si$: 266.1491. Found: 266.1472. Anal. calcd. for $C_{18}H_{22}Si$: C, 81.14; H, 8.32. Found: C, 81.12; H, 8.24. **17c**: 4-$MeOC_6H_4C{\equiv}CSiMe_3$ (0.53 g, 2.6 mmol) was hydroborated (5.2 mL of 1M HBcat in THF) using DMA (0.1 mL) as catalyst in CH_2Cl_2 (10 mL). The solvent was removed *in vacuo* then $Pd(PPh_3)_4$ (78 mg, 0.07 mmol); toluene/ethanol/water (8/8/2 mL); iodobenzene (0.58 mL, 5.2 mmol); and Na_2CO_3 (0.62 g, 5.8 mmol) were added to the residue. The resulting solution was refluxed for 15 hours (overnight) which afforded **3c** (0.11 g, 0.38 mmol) as a colourless oil in 15% yield. ^{1}H NMR ($CDCl_3$): 7.32 (dd, J = 6.0, 7.3 Hz, 2H, C*H*$_{aryl}$); 7.26 (d, J = 8.6 Hz, 2H, C*H*$_{aryl}$); 7.24-7.18 (m, 4H, C*H*$_{aryl}$, =C*H*); 6.89 (d, 2H, C*H*$_{aryl}$); 3.83 (s, 3H, OC*H*$_3$); -0.02 (s, 9H, SiC*H*$_3$). ^{13}C NMR ($CDCl_3$): 158.9, 147.7, 146.2, 132.7 (*C*$_{quat}$); 144.9 (=*C*H); 130.0, 128.2, 127.4, 125.8, 125.8, 113.5 (*C*H$_{aryl}$); 55.4 (O*C*H$_3$); 1.1 (Si*C*H$_3$). Mass spectrum: 282 (24, M^+); 267 (14, M^+-CH_3); 73 (100, $(CH_3)_3Si^+$). Exact mass calcd. for $C_{18}H_{22}OSi$: 282.1440. Found: 282.1418. **17d**: 4-$FC_6H_4C{\equiv}CSiMe_3$ (0.30 g, 1.6 mmol) was hydroborated (3.1 mL of 1M HBcat in THF) using DMA (0.1 mL) as catalyst in CH_2Cl_2 (10 mL). The solvent was removed *in vacuo* then $Pd(PPh_3)_4$ (75 mg, 0.06 mmol); toluene/ethanol/water (8/8/2 mL);, iodobenzene (0.35 g, 3.1 mmol); and Na_2CO_3 (0.56 g, 5.3 mmol) were added to the residue. The resulting solution was refluxed for 4 hours which afforded **17d** (0.11 g, 0.40 mmol) as a colourless oil 26% yield. IR (KBr): 3051 (w); 2957 (m); 1595 (C=C); 1504 (s); 1441 (w); 1252 (m) 1219 (m); 838 (s, TMS); 764 (m); 698 (m). ^{1}H NMR ($CDCl_3$): 7.31 (dd, J = 7.1, 7.7 Hz, 2H, C*H*$_{aryl}$); 7.26 (dd, $^4J_{HF}$ = 5.5 Hz and J = 8.6 Hz, 2H, C*H*$_{aryl}$); 7.21 (t, 1H, C*H*$_{aryl}$); 7.20 (s, 1H, =C*H*); 7.17 (d, 2H, C*H*$_{aryl}$); 7.02 (dd, $^3J_{HF}$ = 8.7 Hz, 2H, C*H*$_{aryl}$); -0.07 (s, 9H, SiC*H*$_3$). ^{13}C NMR ($CDCl_3$): 162.4 (d, $^1J_{CF}$ = 235.8 Hz$_{pso}$F); 147.9, 147.2 (*C*$_{quat}$,); 143.9 (=*C*H); 136.2 (d, $^4J_{CF}$ = 3.8 Hz, C$_{para}$F); 130.4 (d, $^3J_{CF}$ = 8.5 Hz, C$_{meta}$F); 128.2, 127.3, 126.0 (*C*H$_{aryl}$); 115.0 (d, $^2J_{CF}$ = 21.9 Hz, C$_{ortho}$F); 0.9 (Si*C*H$_3$). Mass spectrum: 270 (22, M^+); 255 (16, M^+-CH_3); 196 (46, M^+-$(CH_3)_3$Si-H); 73 (100, $(CH_3)_3Si^+$). Exact mass calcd. for $C_{17}H_{19}FSi$: 270.1241. Found: 270.1231. Anal. calcd for $C_{17}H_{19}FSi$: C, 75.51; H, 7.08. Found: C, 75.53; H, 7.13. (E)-1-phenyl-2-(4-methylphenyl)-2-trimethylsilylethene, **19b**.

(E)-1-phenyl-2-(4-methoxyphenyl)-2-trimethylsilylethene, **19c**.

(E)-1-phenyl-2-(4-fluorophenyl)-2-trimethylsilylethene, **19d**.

These three substrates were prepared using the above procedure from trimethylsilylphenylacetylene and the appropriate aryl bromide. **19b**: Ph$C{\equiv}CSiMe_3$ (0.50 g, 2.9

mmol) was hydroborated (5.8 mL of 1M solution of HBcat in THF) using DMA (0.1 mL) as catalyst in CH_2Cl_2 (10 mL). The solvent was removed *in vacuo* then $Pd(PPh_3)_4$ (23 mg, 0.02 mmol); toluene/ethanol/water (8/8/2 mL); *p*-bromotoluene (0.50 g, 2.9 mmol); and Na_2CO_3 (0.572 g, 5.4 mmol) were added to the residue. The resulting solution was refluxed for 4 hours affording **19b** (0.21 g, 0.81 mmol) in 28% yield as a colourless oil. IR (KBr): 3019 (m); 2955 (s); 1588, 1572 (m, C=C); 1505 (s); 1443 (m); 1248 (s); 838 (vs, TMS); 807 (s); 750 (s); 697 (s). ^{1}H NMR ($CDCl_3$): 7.40-7.28 (m, 5H, C_6H_5); 7.32 (s, 1H, =C*H*); 7.17, 7.15 (AB_q, J = 8.3 Hz, 4H, C_6H_4); 2.40 (s, 3H, CH_3); -0.01 (s, 9H, $SiCH_3$). ^{13}C NMR ($CDCl_3$): 147.3, 144.5, 140.4, and 135.4 (C_{quat}); 145.0 (=*C*H); 128.9, 128.8, 128.1, 127.3, and 127.3 (CH_{aryl}); 21.3 (CH_3); 1.0 ($SiCH_3$). Mass spectrum: 266 (76, M^+); 251 (57, M^+-CH_3); 73 (100, $(CH_3)_3Si^+$). Exact mass calcd. for $C_{18}H_{22}Si$: 266.1491. Found: 266.1477. Anal. calcd for $C_{18}H_{22}Si$: C, 81.14; H, 8.32. Found: C, 81.12; H, 8.24. **19c**: $PhC{\equiv}CSiMe_3$ (1.61 g, 9.2 mmol) was hydroborated (18.4 mL of 1M solution of HBcat in THF) using DMA (0.3 mL) as catalyst in CH_2Cl_2 (10 mL). The solvent was removed *in vacuo* then $Pd(PPh_3)_4$ (88 mg, 0.08 mmol); toluene/ethanol/water (8/8/2 mL); *p*-bromoanisole (2.31 mL, 18.5 mmol); and Na_2CO_3 (2.0 g, 18.9 mmol) were added to the residue. The resulting solution was refluxed for 14 hours which afforded **19c** (0.29 g, 1.1 mmol) in 11% yield as a colourless oil. IR (KBr): 3057 (m); 2954 (s); 1605 (s, C=C); 1506 (vs); 1462 (m); 1442 (s); 1281 (s); 1246 (vs); 1175 (s); 1037 (s); 842 (vs, TMS); 777 (m); 755 (s); 698 (s). ^{1}H NMR ($CDCl_3$): 7.45-7.34 (m, 6H, C_6H_5 and =C*H*); 7.25, 6.98 (d, J = 8.6 Hz, 4H, C_6H_4); 3.88 (s, 3H, OCH_3); 0.08 (s, 9H, $SiCH_3$). ^{13}C NMR ($CDCl_3$): 158.1 (C_{ipso}OMe); 146.8, 140.3, 139.8 (C_{quat},); 144.8 (=*C*H); 128.8, 128.3, 128.0, 127.2, 113.6 (CH_{aryl}); 55.3 (CH_3); 1.0 ($SiCH_3$). Mass spectrum: 282 (91, M^+); 267 (81, M^+-CH_3); 73 (100, $(CH_3)_3Si^+$). Exact mass calcd. for $C_{18}H_{22}OSi$: 282.1440. Found: 282.1423. Anal. calcd. for $C_{18}H_{22}OSi$: C, 76.54; H, 7.85. Found: C, 76.95; H, 8.06. **19d**: $PhC{\equiv}CSiMe_3$ (0.60 g, 3.4 mmol) was hydroborated (6.8 mL of 1M solution of HBcat in THF) using DMA (0.1 mL) as catalyst in CH_2Cl_2 (10 mL). The solvent was removed *in vacuo* then $Pd(PPh_3)_4$ (35 mg, 0.03 mmol); toluene/ethanol/water (8/8/2 mL); *p*-bromofluorobenzene (0.80 mL, 6.9 mmol); and Na_2CO_3 (0.73 g, 6.9 mmol) were added to the residue. The resulting solution was refluxed for 4 hours which afforded **19d** (0.26 g, 0.95 mmol) in 28% yield as a white solid. IR (KBr): 3038 (w); 2956 (m); 1588 (m, C=C); 1501 (s); 1442 (m); 1252 (s); 1219 (s); 1157 (m); 838 (vs, TMS); 753 (s); 696 (s). ^{1}H NMR ($CDCl_3$): 7.33 (m, 5H, C_6H_5); 7.29 (s, 1H, =C*H*); 7.17 (dd, $^4J_{HF}$ = 5.5 Hz, J = 8.7 Hz, 2H, C*H*); 7.03 (dd, J = 8.7 Hz, $^3J_{HF}$ = 8.8 Hz, 2H, C*H*); -0.03 (s, 9H, $SiCH_3$). ^{13}C NMR ($CDCl_3$): 161.5 (d, $^1J_{CF}$ = 251.5 Hz$_{pso}$F); 146.5, 140.0 (C_{quat}); 145.5 (=*C*H); 143.3 (d, $^4J_{CF}$ = 3.9 Hz, C_{para},); 128.8 (d, $^3J_{CF}$ = 8.1 Hz, C_{meta}H); 115.0 (d, $^2J_{CF}$ = 21.4 Hz, C_{ortho}); 128.8, 128.1, 127.4 (C_6H_5); 0.8 ($SiCH_3$). Mass spectrum: 270 (73, M^+); 255 (62, M^+-CH_3); 73 (100, $(CH_3)_3Si^+$). Exact mass calcd. for $C_{17}H_{19}FSi$: 270.1240. Found: 270.1215. Anal. calcd. for $C_{17}H_{19}FSi$: C, 75.51; H, 7.08. Found: C, 75.59; H, 7.26.

4.11 Hydroboration of (E)-1-phenyl-1-trimethylsilyl-2-(4-X-phenyl)ethenes, ***17b-d.***

Vinylsilanes **17b-d** were added to a suspension of **1** in C_6D_6 and the products **18b-d** assayed by NMR spectroscopy. **17b** (25.0 mg, 0.094 mmol) and **1** (32.0 mg, 0.094 mmol) gave borane

18b. NMR data for **18b**: ^{1}H: 7.28, 6.89 (d, J = 7.9 Hz, 4H, C_6H_4); 6.85 (m, 4H, $CH_{meta,ortho}$); 6.75 (t, J = 6.9 Hz, 1H, CH_{para}); 4.53 (d, J = 12.8 Hz, 1H, BC*H*); 2.96 (d, 1H, SiC*H*); 1.95 (s, 3H, CH_3); -0.30 (s, 9H, $SiCH_3$). ^{13}C: 144.6, 137.5, 134.8 (C_{ipso}); 130.7, 130.3, 128.5, 127.7, 125.0 (CH_{aryl}); 50.1 (B*C*H); 38.1 (Si*C*H); 20.8 (CH_3); -2.0 ($SiCH_3$). ^{19}F: -130.5 (F_o); -149.9 (F_p); -161.6 (F_m). ^{11}B: 78.5 (1790). **17c** (22.0 mg, 0.078 mmol) and **1** (27.1 mg, 0.078 mmol) gave borane **18c**. NMR data for **18c**: ^{1}H: 7.25, 6.67 (d, J = 8.6 Hz, 4H, C_6H_4); 6.86 (m, 4H,$CH_{meta,ortho}$); 6.76 (t, J = 7.1 Hz, 1H, CH_{para}); 4.51 (d, J = 12.9 Hz, 1H, BC*H*); 3.18 (s, 3H, OCH_3); 2.92 (d, 1H, SiC*H*); -0.29 (s, 9H, $SiCH_3$). ^{13}C: 159.7, 144.7, 128.8 (C_{ipso}); 132.1, 128.5, 127.6, 125.0, 115.1 (CH_{aryl}); 54.7 (OCH_3); 49.4 (B*C*H); 38.2 (Si*C*H); -2.0 ($SiCH_3$). ^{19}F: -130.5 (F_o); -149.9 (F_p); -161.7 (F_m). ^{11}B: 72.5 (3640). **17d** (32.0 mg, 0.118 mmol) and **1** (41.0 mg, 0.118 mmol) gave borane **18d**. NMR data for **18d**: ^{1}H: 7.12 (dd, $^{4}J_{HF}$ = 5.3 Hz and J = 8.5 Hz, 2H, C_6H_4); 6.84 (m, J = 7.1 Hz, 2H, CH_{meta}); 6.78 (m, 1H, CH_{para}); 6.74 (d, 2H, CH_{ortho}); 6.69 (dd, $^{3}J_{HF}$ = 8.5 Hz, 2H, C_6H_4); 4.44 (d, J = 12.9 Hz, 1H, BC*H*); 2.83 (d, 1H, SiC*H*); -0.37 (s, 9H, $SiCH_3$). ^{13}C: 162.4 (d, $^{1}J_{CF}$ = 247.0 Hz, FC_{ipso}); 144.2 (C_{ipso}); 133.7 (d, $^{4}J_{CF}$ = 2.6 Hz, C_{ipso}); 132.1 ($^{3}J_{CF}$ = 7.6 Hz, CH_{aryl}); 128.6, 127.6, 125.1 (CH_{aryl}); 116.4 (d, $^{2}J_{CF}$ = 21.6 Hz, CH_{aryl}); 49.4 (B*C*H); 38.1 (Si*C*H); -2.1 ($SiCH_3$). ^{19}F: -114.0 (C*F*); -130.6 (F_o); -149.4 (F_p); -161.5 (F_m). ^{11}B: 74.8 (1930).

4.12 Hydroboration of (E)-1-phenyl-2-(4-X-phenyl)-2-trimethylsilylethenes, ***19b-d***.

Vinylsilanes **19b-d** were added to a suspension of **1** in C_6D_6 and the product **20b-d** assayed by NMR spectroscopy. **19b** (30.0 mg, 0.113 mmol) and **1** (39.0 mg, 0.113 mmol) gave borane **20b**. NMR data for **20b**: ^{1}H: 7.33 (d, J = 7.6 Hz, 2H, CH_{ortho}); 7.02 (m, 2H, CH_{meta}); 6.91 (t, J = 7.4 Hz, 1H, CH_{para}); 6.70 (m, 4H, C_6H_4); 4.51 (d, J = 12.9 Hz, 1H, BC*H*); 2.94 (d, 1H, SiC*H*); 2.01 (s, 3H, CH_3); -0.31 (s, 9H, $SiCH_3$). ^{13}C: 141.3, 138.5, 134.6 (C_{ipso}); 130.6, 129.5, 129.2, 127.7, 127.6 (CH_{aryl}); 50.8 (B*C*H); 37.6 (Si*C*H); 20.5 (CH_3); -2.0 ($SiCH_3$). ^{19}F: -130.5 (F_o); -149.9 (F_p); -161.8 (F_m). ^{11}B: 77.1 (1830). **19c** (36.0 mg, 0.127 mmol) and **1** (44.0 mg, 0.127 mmol) gave borane **20c**. NMR data for **20c**: ^{1}H: 7.34 (d, J = 7.5 Hz, 2H, CH_{ortho}); 7.04 (m, 2H, CH_{meta}); 6.92 (t, J = 7.4 Hz, 1H, CH_{para}); 6.74, 6.50 (d, J = 8.5 Hz, 4H, C_6H_4); 4.49 (d, J = 12.9 Hz, 1H, BC*H*); 3.29 (s, 3H, OCH_3); 2.94 (d, 1H, SiC*H*); -0.29 (s, 9H, $SiCH_3$). ^{13}C: 157.8, 139.2, 136.0 (C_{ipso}); 130.6, 139.4, 128.6, 127.6, 115.5 (CH_{aryl}); 54.8 (OCH_3); 52.4 (B*C*H); 38.3 (Si*C*H); -0.6 ($SiCH_3$). ^{19}F: -130.6 (F_o); -149.9 (F_p); -161.8 (F_m). ^{11}B: 74.9 (1930). **19d** (15.6 mg, 0.058 mmol) and **1** (20.0 mg, 0.058 mmol) gave borane **20d**. NMR data for **20d**: ^{1}H: 7.28 (d, J = 7.6 Hz, 2H, CH_{ortho}); 7.01 (m, 2H, CH_{meta}); 6.90 (t, J = 7.4 Hz, 1H, CH_{para}); 6.60 (br m, 2H, C_6H_4); 6.54 (dd, $^{3}J_{HF}$ = 8.3 Hz and J = 8.4 Hz, 2H, C_6H_4); 4.41 (d, J = 12.9 Hz, 1H, BC*H*); 2.86 (d, 1H, SiC*H*); -0.38 (s, 9H, $SiCH_3$). ^{13}C: 160.9 (d, $^{1}J_{CF}$ = 244.0 Hz, FC_{ipso}); 139.9 (d, $^{4}J_{CF}$ = 2.6 Hz, C_{ipso}); 137.8 (C_{ipso}); 130.7, 129.5, 129.5 (CH_{aryl}); 127.8 (d, $^{3}J_{CF}$ = 7.2 Hz, CH_{aryl}); 115.3 (d, $^{2}J_{CF}$ = 20.9 Hz, CH_{aryl}); 50.6 (B*C*H); 37.2(Si*C*H); -2.1 ($SiCH_3$). ^{19}F: -117.7 (C*F*); -130.5 (F_o); -149.1 (F_p); -161.3 (F_m). ^{11}B: 74.7 (1730).

*4.13 Thermolysis of Boranes **13, 16, 18b-d** and **20b-d**.*

Solutions of these boranes were generated as described above and loaded into sealable 5 mm NMR tubes. The tubes were flame sealed and placed in a thermostated oil bath set to temperatures of between 80 and 120°C depending on the substrate. The progress of the rearrangements were monitored by ^{1}H NMR spectroscopy.

4.14 Reaction of in situ Generated Lithium Bis-(pentafluorophenyl)phenyl-(E)-2-phenylethenylborate with Trimethylsilyl Triflate.

Phenylacetylene (16 μL, 0.145 mmol) was added to a suspension of **1** (50 mg, 0.145 mmol) in C_6D_6 (0.5 mL). When all of **1** had dissolved, phenyl lithium (12 mg, 0.145 mmol) was added to the solution and the reaction was stirred for 30 minutes. The reaction mixture was placed in a 5 mm NMR tube capped with a septum and the sample was heated to reflux temperature for 5 minutes. The ^{1}H NMR spectrum at this point indicated that the product of phenylacetylene hydroboration was completely consumed and a new product present. Addition of TMSOTf (29 μL, 0.145 mmol) led to an immediate precipitation of a gelatinous white solid. The sample was filtered to remove the precipitate, then the ^{1}H NMR spectrum and GC/MS of the sample were obtained, indicating the presence of (E)-1-trimethylsilyl-2-phenylethene and borane **14** as major components. Resonances for a minor product are consistent with the diastereomer of borane **13**.

4.15 Calculations

All structures were built using the SPARTAN molecular modeling program[30]. All structures were geometry-optimized using semi-empirical methods at the AM1 level of theory. Preliminary transition state structures were obtained by averaging the geometry-optimized reactant and product structures. The key atoms were fixed in position and the entire structure was geometry-optimized under those constraints. The geometry-optimized structure was submitted for transition state calculation with no restraints. The search led to a saddle point on the potential energy surface which was confirmed as a legitimate transition structure by frequency analysis, showing an imaginary frequency with a vibration corresponding to the movement along the reaction coordinate. Charges were calculated at the AM1 level using Mulliken population analysis.

5. Acknowledgments. Funding for this work from the Natural Sciences and Engineering Research Council of Canada in the form of a Research Grant to WEP and Scholarship support to DJP (1994-98). WEP also thanks the Alfred P. Sloan Foundation for a Research Fellowship (1996-2000).

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